In a recent publication Tobolsky and Gupta (1) have treated a succession of n segments in an isolated polymer molecule which has randomly coiled regions and ordered helical (crystalline) regions as a Markov chain. The molecular chains trace out a path on a cubic crystal lattice. The chain passes through amorphous regions in which the link vectors of the chain successively point in the three three-dimensional directions \((\pm x, \pm y, \pm z)\). The chain vector also passes through crystalline regions which for simplicity we assume to have preferred directions only along the \(+x\), \(+y\), \(+z\) axes. A +x crystal region is one in which the chain progresses in the +x direction but in which the y and z chain vectors are symmetrically spiralled so that the net contribution of the y and z components over the entire +x crystal is zero. We take the length of each link in the amorphous or crystalline regions to be unity, using as our unit of distance the quantity \(1/\sqrt{3}\) where l, the bond length, is taken as the root-mean-square length of a triad of successive x, y, z links. Similar discussion holds for crystals in other possible directions.
The succession of the $\pm x$ linkages of the polymer chain form a Markov chain, if we consider the elements of the chain to have five possible states $r_+, r_-, h_+, h_-$ and $h_0$. The $r_+$ denotes an $x$ link in the amorphous region pointing in the $+1$ direction, $r_-$ denotes an $x$ link in the amorphous region in the $-1$ direction, $h_+$ denotes an $x$ link in the $+x$ crystal, $h_-$ denotes an $x$ link in the $-x$ crystal and $h_0$ and $x$ link in a $\pm y$ or $\pm z$ crystal.

The progress of the chain with orientation parameter $\beta$ in the $x$ direction is given by the transition probability matrix (1):

$$
\begin{array}{cccccc}
& r_+ & r_- & h_+ & h_- & h_0 \\
r_+ & \frac{1}{2}(1-p) & \frac{1}{2}(1-p) & p\beta & 0 & (1-\beta)p \\
r_- & \frac{1}{2}(1-p) & \frac{1}{2}(1-p) & 0 & p\beta & (1-\beta)p \\
h_+ & 1-\alpha & 0 & \alpha & 0 & 0 \\
h_- & 0 & 1-\alpha & 0 & \alpha & 0 \\
h_0 & \frac{1}{2}(1-\alpha) & \frac{1}{2}(1-\alpha) & 0 & 0 & \alpha \\
\end{array}
$$

In the foregoing treatment the orientation in the amorphous region is completely ignored. However, there are polymers which exhibit orientation in amorphous region also as has been experimentally observed in x-ray studies (2) on polyethylene samples. In the present communication we report a modification of the Tobolsky - Gupta model by including
orientation in the amorphous region as well. Now the transition probability matrix is given by as

<table>
<thead>
<tr>
<th></th>
<th>$r_+$</th>
<th>$r_-$</th>
<th>$h_+$</th>
<th>$h_-$</th>
<th>$h_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_+$</td>
<td>$(1-p)^\mu$</td>
<td>$(1-p) (1-\mu)$</td>
<td>$\beta p$</td>
<td>0</td>
<td>$(1-\beta)p$</td>
</tr>
<tr>
<td>$r_-$</td>
<td>$(1-\mu)$</td>
<td>$(1-p)^\mu$</td>
<td>0</td>
<td>$p\beta$</td>
<td>$(1-\beta)p$</td>
</tr>
<tr>
<td>$h_+$</td>
<td>$1-\alpha$</td>
<td>0</td>
<td>$\alpha$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$h_-$</td>
<td>0</td>
<td>$1-\alpha$</td>
<td>0</td>
<td>$\alpha$</td>
<td>0</td>
</tr>
<tr>
<td>$h_o$</td>
<td>$\frac{1-\alpha}{2}$</td>
<td>$\frac{1-\alpha}{2}$</td>
<td>0</td>
<td>0</td>
<td>$\alpha$</td>
</tr>
</tbody>
</table>

Here an extra parameter $\mu$ is introduced which denotes the orientation in the amorphous region.

The expected square of the end-to-end distance in the $x$ direction is given by (The mathematical details are given in the appendix)

$$\langle R_x^2 \rangle = n \left[ \frac{(1-\alpha + \beta p) (2-2\mu - \beta p + \beta p + 2\mu p)}{(1-\alpha + p) (2-2\mu - \beta p + 2\mu p)} \right] + \frac{2p (2-\alpha)\beta}{(1-\alpha) (1-\alpha + p) (2-2\mu - \beta p + 2\mu p)} + \frac{2(\mu+1) - 1 - 2\mu p}{(1-\alpha) (1-\alpha + p) (2-2\mu - \beta p + 2\mu p)} \cdot \frac{2}{3} \cdot \frac{1}{3} \cdot \frac{1}{3} \quad \text{(3)}$$

For $\mu = 2$, it reduces to the expression reported in reference (1) for a chain with no orientation or equal orientation in the amorphous part.
The fractional crystallinity (or helicity) and amorphicity remain unchanged. The uninterrupted sequence lengths \( \bar{r}_+ \) in the amorphous region are given by

\[
\bar{r}_+ = \lim_{n \to \infty} \sum_{n-1} \left[ \mu(1-p) \right]^{n-1} \left[ 1-(1-p)/\mu \right]
\]  

or

\[
\bar{r}_+ = \frac{1}{1-\mu(1-p)} = \bar{r}_-
\]

Similarly \( \bar{h}_+ = \bar{h}_- = \frac{1}{1-\alpha} \)

where \( \bar{h}_+ \) and \( \bar{h}_- \) are the uninterrupted sequence lengths in the + and - crystals respectively.

**APPENDIX**

If the length of successive vectors along the + direction be \( x^{(o)}, x^{(1)}, x^{(2)}, \ldots, x^{(n-1)} \), the expected square of the end-to-end distance is given by

\[
R_{x}^{2} = (x^{(o)} + x^{(1)} + x^{(2)} + \ldots + x^{(n-1)})^{2}
\]

\[
< R_{x}^{2} > = n E^{(1)} + 2 \sum_{k=1}^{n-1} (n-k) L_{k}
\]

where \( L_{k} = E (x^{o} - x^{k}) \)

As explained in the text, the value of each vectors in the unit of length \( 1/\sqrt{3} \) is \( \pm 1 \) and the successive x components are related by a Markoff formalism.
The value of $L_k$ in this sense can be written as

$$L_k = \sum_{k} p_{11}^k - p_{12}^k + p_{13}^k - p_{14}^k \cdots \quad (7)$$

where $P$'s are the elements in the first row of the $k$th power of the matrix and it is assumed that the chain started in $r_+$ state. We calculate individually the expected squares of the end-to-end distance for the chain starting in $r_+$, $h_+$ and $h_0$ states, weigh them according to steady-state probabilities and finally combine to get $\langle R_x^2 \rangle$. Thus if $\langle R_{x1}^2 \rangle$, $\langle R_{x2}^2 \rangle$, $\langle R_{x3}^2 \rangle$, $\langle R_{x4}^2 \rangle$ and $\langle R_{x5}^2 \rangle$ be the five values for the chain starting in $r_+$, $r_-$, $h_+$, $h_-$ and $h_0$ states respectively.

$$\langle R_x^2 \rangle = \frac{\langle R_{x1}^2 \rangle}{\beta_p} + \frac{\langle R_{x2}^2 \rangle}{\beta_p} + \frac{\langle R_{x3}^2 \rangle}{\beta_p} + \frac{\langle R_{x4}^2 \rangle}{\beta_p} + \frac{\langle R_{x5}^2 \rangle}{\beta_p} \quad \cdots (8)$$

The steady-state probabilities given by the relation $\beta_p = \frac{1}{\alpha}$ are

$$\frac{1 - \alpha}{2(1 - \alpha + p)}$$

for the $r_+$ and $r_-$ states.

$$\frac{\beta_p}{2(1 - \alpha + p)}$$

for the $h_+$ and $h_-$ states.

and

$$\frac{p(1 - \beta_p)}{(1 - \alpha + p)}$$

for the $h_0$ state.

and also

$$E(x \pm 1) = \frac{(1 - \alpha + \beta_p p)}{(1 - \alpha + p)}$$
Thus
\[
\langle R_{x_1}^2 \rangle = \frac{1 - \alpha}{2(1 - \alpha + p)} \left[ \sum_{k=1}^{n-1} \left( 1 - \frac{\alpha + p}{1 - \alpha + p} \right) L_{k1} \right] \ldots \ldots (9)
\]

Here
\[
L_{k1} = p_{11}^k - p_{12}^k + p_{13}^k - p_{14}^k \ldots (10)
\]

Similar expressions can be written for the other four cases.

The matrix (1) has eigen values \( \lambda', \lambda, \lambda - p, \lambda' \) and \( \lambda'' \)

where \( \lambda' \) and \( \lambda'' \) are the roots of the quadratic equation

\[
\lambda^2 - \lambda (\alpha + 2\mu - 2p) - \beta p + \alpha(\mu p + 3\mu - 2\mu' - \mu') = 0
\]

and are given by

\[
\lambda' + \lambda'' = \alpha + 2\mu - 2p + p - 1
\]

\[
\lambda' \lambda'' = p(\alpha \beta - \beta + \alpha(\mu - 1) + \alpha(2\mu' - 1) - 2\mu' \mu')
\]

\n
nth state probabilities of the transition probability matrix

are given below

\[
\begin{align*}
p_{11}^k &= p_{22}^k = \frac{L}{2(1 - \alpha + p)} + \frac{\Delta \lambda^{k+1} - \alpha \lambda^k}{2 \Delta \lambda}, \\
p_{12}^k &= p_{21}^k = \frac{L}{2(1 - \alpha + p)} + \frac{\Delta \lambda^{k+1} - \alpha \lambda^k}{2 \Delta \lambda}, \\
p_{13}^k &= p_{24}^k = \frac{\beta p L^{k-1}}{2(1 - \alpha + p)} + \frac{\beta p \Delta \lambda^k}{2 \Delta \lambda}, \\
p_{14}^k &= p_{23}^k = \frac{\beta p L^{k-1}}{2(1 - \alpha + p)} + \frac{\beta p \Delta \lambda^k}{2 \Delta \lambda}, \\
p_{21}^k &= p_{42}^k = \frac{(1 - \alpha) L^{k-1}}{2(1 - \alpha + p)} + \frac{(1 - \alpha) \Delta \lambda^k}{2 \Delta \lambda}
\end{align*}
\]
\[ p_{15} = p_{25} = \frac{(1-\beta) P L}{(1-\alpha + p)} \]

\[ p_{32} = p_{41} = \frac{(1-\alpha) L}{2(1-\alpha + p)} - \frac{(1-\alpha) \Delta \lambda^k}{2 \Delta \lambda} \]

\[ p_{33} = p_{44} = \frac{\beta L}{2(1-\alpha + p)} + \frac{(1-\beta) \alpha^k}{2} + \frac{\lambda \Delta \lambda^k - \lambda' \lambda'' \Delta \lambda^k - 1}{2 \Delta \lambda} \]

\[ p_{34} = p_{43} = \frac{\beta L}{2(1-\alpha + p)} + \frac{(1-\beta) \alpha^k}{2} - \frac{\lambda \Delta \lambda^k - \lambda' \lambda'' \Delta \lambda^k - 1}{2 \Delta \lambda} \]

where

\[ L = (1-\alpha) + p(\alpha - p)^k \]

\[ L'' = 1 - (\alpha - p)^k \]

\[ L''' = \beta + (1-\alpha) (\alpha - \beta)^k \]

and \( \Delta \) is operator \( \lambda' - \lambda'' \)

Substituting the various terms in equation (7)

\[ \Delta \lambda^k + \frac{1 - \alpha \Delta \lambda^k}{\Delta \lambda} + \frac{\beta p \Delta \lambda^k}{\Delta \lambda} \]

Note that

\[ \sum_{k=1}^{n-1} (n-k) \lambda^k = \frac{n \lambda}{1-\lambda} + \frac{\lambda^{n+1}}{(1-\lambda)^2} - \frac{\lambda}{(1-\lambda)^2} \quad \ldots (11) \]

and

\[ \sum_{k=1}^{n-1} (n-k) \lambda^{k+1} = \frac{n \lambda^2}{1-\lambda} + \frac{\lambda^{n+2}}{(1-\lambda)^2} - \frac{\lambda^2}{(1-\lambda)^2} \quad \ldots (12) \]

Making use of the equations (11) and (12) and keeping only the leading terms, we have
\[
\sum_{k=1}^{n-1} (n-k) L_{k1} = \left[ \frac{1-\alpha}{(1-\alpha)(2-2\mu - p - \beta_p + 2\mu p)} \right] \\
\left\{ \frac{(1-\alpha)}{(1-\alpha)(2-2\mu - p - \beta_p + 2\mu p)} \right\}
\]

Substituting this equation in equation (8) we have

\[
\langle R_{x1}^2 \rangle = \frac{n(1-\alpha)}{2(1-\alpha + p)} \left[ \frac{(1-\alpha)^2 + \beta_p}{(1-\alpha + p)} \right]
\]

\[
2 \left\{ \frac{(1-\alpha)(2\mu + p - 1 - 2\mu p + \beta_p (2-2\mu p + 2\mu p)}{(1-\alpha)(2-2\mu - p - \beta_p + 2\mu p)} \right\}
\]

Calculations show

\[
\langle R_{x1}^2 \rangle = \langle R_{x2}^2 \rangle
\]

\[
\langle R_{x3}^2 \rangle = \langle R_{x4}^2 \rangle = \frac{n \beta_p}{2(1-\alpha + p)} \left[ \frac{(1-\alpha + \beta_p)}{(1-\alpha + p)} \right]
\]

\[
2 \left\{ \frac{1+\beta_p (1-\alpha) - \alpha (2\mu - 1 + p) + 2\mu \beta_p}{(1-\alpha)(2-2\mu - p - \beta_p + 2\mu p)} \right\}
\]

and

\[
\langle R_{x5}^2 \rangle = \frac{n \beta_p (1-\beta)}{1-\alpha + p} \left[ \frac{1+\beta_p}{1-\alpha + p} \right]
\]

Substituting these values of \( \langle R_{x1}^2 \rangle \), \( \langle R_{x2}^2 \rangle \), \( \langle R_{x3}^2 \rangle \), \( \langle R_{x4}^2 \rangle \), and \( \langle R_{x5}^2 \rangle \) in equation (8), we finally get

\[
\langle R_{x}^2 \rangle = \frac{n \left[ \frac{(1-\alpha + \beta_p)}{(1-\alpha + p)} \right]}{(1-\alpha)(1-\alpha + p)} \left( \frac{2\mu + p + \beta_p + 2\mu p}{(2-2\mu - p - \beta_p + 2\mu p)} \right)
\]

\[
+ \frac{2\beta_p (2-\alpha)}{(1-\alpha)(1-\alpha + p)(2-2\mu - p - \beta_p + 2\mu p)}
\]

\[
+ \frac{2(p + 2\mu - 1 - 2\mu p) \left\{ (1-\alpha)^2 - \alpha \beta_p \right\}}{(1-\alpha)(1-\alpha + p)(2-2\mu - p - \beta_p + 2\mu p)}
\]
This is independent of the initial state. This has to be scaled by a factor $1^2/3$ and therefore

$$\langle R_x^2 \rangle = n \left[ \frac{(1-\alpha + \beta p)}{(1-\alpha + p)} \right] \frac{(2-2 \mu - p + \beta p + 2 \mu p)}{(2-2 \mu - p - \beta p + 2 \mu p) + \frac{2 \beta p (2 - \alpha)}{(1-\alpha)^2 (1-\alpha + p)} \left[ \frac{(1-\alpha)^2 - \alpha \beta p}{(2-2 \mu - p - \beta p + 2 \mu p)^3} \right] \right]$$

which is the same as equation (3) in the text.

REFERENCES